High Temperature X-Ray Diffraction Techniques*
for Active Metals

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In a study of the properties of rare-earth metals in this laboratory, a high temp transformation was observed in most of these metals near their melting points.¹ High temperature heat capacity measurements

¹ F. H. Spedding and A. H. Daane, J. Metals, 6, 504 (1954).

showed the energy of this transformation to be quite large, ranging from 0.6 to 0.7 entropy units/mole (~700 calorie/mole) compared to entropies of fusion of 1.9 eu/mole,² and electrical resistivity

² F. H. Spedding, J. J. McKeown and A. H. Daane, J. Phys. Chem., 64, 289 (1960).

measurements showed a 10% change at this transformation for some metals.³ By analogy with several other metals that are in close

³ F. H. Spedding, K. W. Herrmann and A. H. Daane, J. Metals, 9, 895 (1957).

packed structures at room temperature and exhibit transformations at

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higher temperatures (Ti, Zr, Th), it was thought that the rare earths might have bcc high temperature structures. Attempts to obtain the bcc form at room temperature by quenching were not successful however,³ and a direct x-ray diffraction study of these metals in the temperature region of the unknown structure was desired.

Due to the very reactive nature of these metals it was not possible to obtain diffraction patterns of their structures at elevated temperatures⁴

⁴ K. W. Herrmann, PhD Thesis, Iowa State University, Ames, Iowa (1956).

using a diffractometer designed for this purpose.⁵ In such attempts, it

⁵ P. Chiotti, Rev. Sci. Instr., 25, 683 (1954).

was found that adsorbed gases in the camera were released as the sample was heated, and only diffraction patterns of reaction products of these gases with the metals were observed. The techniques described below were devised to eliminate this problem.

CAMERA

A 57.3 cm diameter camera, manufactured by Otto von der Heyde and described by Buerger et al,⁶ designed to operate up to 600°C, was

⁶ M. J. Buerger, N. W. Buerger and F. G. Chesley, Am. Mineralogist, 28, 285 (1943).

modified for use in this study. The original collimator was replaced by

one having a circular slit of only 0.018" diameter and which extended to within 1/4" of the specimen. This reduced scattered radiation in the camera.

TECHNIQUE FOR TEMPERATURES UP TO 100°C

The original furnace in the camera was replaced by the furnace shown in Fig. 1. The two concentric cylinders were machined out of Lava* and then fired at 1200°C for 24 hrs. The outer surface of the smaller cylinder was grooved to receive the heating element which consisted of 4 feet of 0.010" platinum-13% rhodium wire, and the entire assembly could be inserted into the original metal housing of the camera. This furnace maintained a temperature of 1000°C on a power consumption of 160 watts. A Pt-13% Rh thermocouple was placed in the furnace as shown, with its junction within 0.1" of the x-ray specimen. The thermocouple was calibrated by measuring the lattice constants of a sample of pure silver as a function of temperature as described by Hume-Rothery and Reynolds,⁷ with an average deviation of the observed

⁷ W. Hume-Rothery and P. W. Reynolds, Proc. Roy. Soc. (A), 167, 25 (1938).

lattice constants that indicated an uncertainty of $\pm 7^\circ\text{C}$ in the sample temperature.

To prepare the x-ray samples, a small piece of the metal was rolled to a thickness of 0.007", and wires of rectangular cross section were sheared off. These were scraped with a surgical scalpel to obtain

* A soapstone product of the American Lava Corp., Chattanooga, Tenn.

Fig. 1—X-ray Camera Furnace.

cylindrical specimens 0.004" thick which were cut to lengths of 0.25" weighing about 0.8 mg. Tungsten spacers were prepared from the filament of a 200 watt Sylvania light bulb. A 3 mm long piece of this filament was threaded onto a 0.010" tungsten wire, and the open end of the filament segment was welded shut with a Heliarc welder. Two of these spacers were slipped onto the ends of the x-ray specimen which was placed in a silica x-ray capillary 0.5 mm in diameter. The capillary was connected to a high vacuum system by means of Apiezon-W wax, and while maintaining a vacuum in the system of 5×10^{-7} mm, the sample was first warmed to 400°C to outgas it and was then sealed off as shown in Fig. 2. The quartz specimen holder, previously attached to the closed end of the capillary, is shown in Fig. 3. This was clamped in the specimen holder of the camera and was centered in the furnace and rotated during the exposure by the original camera mechanism. For some of the more reactive rare-earth metals (La, Ce, Pr, Nd, Eu), the samples were shaped and encapsulated in a scavenged, helium atmosphere; such precautions were not necessary with the other rare-earth metals. With such specimens, good diffraction patterns of these metals were obtained in 1 1/2 hrs. at temperatures up to 1000°C.

TECHNIQUE FOR TEMPERATURES UP TO 2200°C

To study the rare-earth metals whose high temperature transformation was above 1000°C, the following technique was devised. A copper tube was machined as shown in Fig. 4. The slot parallel to the axis of

Fig. 2—Metal Specimen Supported by Tungsten Spacers in X-ray Capillary, 15X.

Fig. 3—X-ray Specimen on Silica Support, 4X.

SCALE : 2" = 1"

Fig. 4—High Temperature Specimen Chamber.

the tube allowed access to the specimen mounting posts, while the slot extending nearly around the tube at right angles to the axis of the tube permitted the incident x-ray beam to strike the specimen and the diffracted beam to pass out to the film. The specimens were about 0.005" diameter and were formed from slivers sheared from rolled sheets of the metals as described above. The hollow connector extending out through the Stupakoff seal served both as an electrical lead to one end of the specimen and as a connection to the high vacuum system. After mounting the specimen the chamber is made vacuum tight by the following procedure. The slots in the copper tube are covered with masking tape, trimmed to provide 1/16" extension onto the copper base. The surface of the copper tube is then given a light coat of Krylon* clear plastic spray from a pressure can dispenser, and the masking tape is immediately removed. A precut piece of 0.0005" Saran Wrap plastic** is applied to the cylinder to cover it from end to end and to give an overlap of 1/16" to 1/8". The Saran Wrap must be applied within 5 seconds after the Krylon is applied to the surface in order to give a good bond to the base. The assembly is then placed in a drying oven at 100°C for 3 to 5 minutes to give a good seal between the Saran Wrap and the copper tube. This process also serves to shrink the Saran Wrap over the slotted areas and results in a tightly stretched film that is surprisingly vacuum tight and also transparent and rather durable to x-rays. In this shrinking operation none of the more active metals were corroded so as to prevent

* An acrylic resin in a mixture of chlorinated and aromatic hydrocarbon solvents, Krylon, Inc., Norristown, Pa.

** A product of the Dow Chemical Co., Midland, Mich.

their study, although in the case of europium, care was taken to exclude moisture and to prevent more than a minimum of exposure to air.

The assembly (Fig. 5) is mounted in the camera and is connected to a high vacuum system by means of a rubber tube that is greased inside and out with Apiezon-W grease to prevent diffusion of air into the system. The specimen cannot be rotated completely as this would bring the unslotted portion of the copper tube into the x-ray beam; also, the vacuum and electrical connections would be more complicated. Consequently, the assembly is positioned in the beam with the unslotted portion of the tube at the top, as shown in Fig. 6. A "four bar linkage" connecting the pulley of the camera with that of the motor in the base of the camera mount on the x-ray source unit then provides for an oscillatory motion of the specimen. The ends of the assembly are connected to a 6 volt electrical supply with a 10 ohm slide wire resistor in series to regulate the current. With the rare-earth metals, which have high resistivities ($50-70 \times 10^{-6}$ ohm-cm at room temperature), a current of one ampere will achieve a temperature of about 1100°C in this apparatus. After a vacuum of 1×10^{-6} mm is indicated in the vacuum system for 15 minutes, gentle outgassing of the specimen and its surroundings is accomplished by gradually increasing the current through the specimen. When the desired temperature is reached, the specimen is recentered in the x-ray beam since thermal expansion usually moves the specimen out of the beam from the room temperature adjustment. To shorten the exposure time in this work, the nickel filter is removed from the copper x-ray beam since the patterns are so simple that

Fig. 5—High Temperature Chamber with Saran Window in Place.

Fig. 6—High Temperature Chamber in Place in Camera.

identification of the beta lines is easy. Even with the precautions observed, there is usually a small amount of a non-metallic impurity that gets to the specimen and the results in several spurious lines in the diffraction pattern. These lines are easily identified, as the compounds are refractory enough to resist grain growth and give rather soft continuous lines on the film, whereas the metal experiences a great deal of recrystallization and grain growth and gives a very spotty pattern. With this technique, a diffraction pattern of the metal may be obtained in about 20 minutes. To reduce diffusion of air into the sample chamber, the open end of the camera is covered with aluminum foil and a positive pressure of helium is maintained inside the camera.

The temperature of the specimen may be determined by a direct reading with an optical pyrometer, with due corrections for emissivity and absorption in the lead glass window on the beam catcher. A second method is particularly useful when it is desired to heat the specimen into the temperature region of stability of a particular phase; a potentiometer is connected across the specimen, and the resistivity of the specimen is observed. As the resistivity of the rare-earth metals changes very significantly (about 10%) on transforming to the body-centered-cubic form, it is easy to adjust the temperature to get the metals into this structure.

As is reported in detail elsewhere,⁸ the high temperature body-

⁸ F. H. Spedding, J. J. Hanak and A. H. Daane, paper submitted to J. Less Common Metals (1960).

centered-cubic form of several of the rare-earth metals has been

characterized by these techniques. Because of experimental difficulties, it was not possible to get lattice constants of the body-centered-cubic forms with more precision than $\pm 0.01\text{\AA}$. In the case of the samples in the quartz capillaries, there was a reaction that resulted in a progressive deterioration of both the sample and the capillary, and longer exposures gave few lines in the back reflection region. With the samples heated by their own resistance in the copper tube furnace, the Saran Wrap windows gradually deteriorated from thermal and x-ray radiation and would eventually rupture; also, as the specimens were attacked by the residual gases in the furnace, their resistivities changed and made temperature control difficult, resulting in broader lines.

In the case of the lower temperature forms of these metals, it was not difficult to get lattice constants to within $\pm 0.001\text{\AA}$. This made it possible to determine the thermal expansion coefficient of these metals along the separate crystallographic axis as has been described.⁸

To observe the operation of these x-ray techniques at higher temperatures, diffraction patterns were obtained of tungsten at 1880°C and 2190°C , and these data are shown with lower temperature data in Fig. 7. The mean coefficient of expansion at 2035°C calculated from the two lattice constants was $12 \times 10^{-6}^{\circ}\text{C}^{-1}$. The quality of the diffraction patterns of tungsten was significantly better than that of the rare-earth metals, and afforded lattice constants of greater precision to make this data possible.

Fig. 7—Lattice Constant of Tungsten at High Temperatures.